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(54) A self-reinforced silicon nitride ceramic of high fracture toughness and a method of preparing the same.

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Description

This invention pertains to a silicon nitride (Si_3N_4) ceramic body and a process for preparing the ceramic body.

Silicon nitride ceramics are recognized for their excellent mechanical and physical properties, including good wear resistance, low coefficient of thermal expansion, good thermal shock resistance, high creep resistance and high electrical resistivity. In addition, silicon nitride ceramics are resistant to chemical attack, particularly to oxidation. Because of these attributes, silicon nitride is useful in a variety of wear and high temperature applications, such as cutting tools and parts in pumps and engines.

Failure of silicon nitride ceramics is generally associated with brittleness and flaws. The object therefore is to prepare a silicon nitride ceramic with high fracture toughness (K_{IC}) and strength. Fracture strength is directly proportional to the fracture toughness and inversely proportional to the square root of the flaw size. High fracture toughness combined with small flaw size is therefore highly desirable. Monolithic silicon nitride, however, has a relatively low fracture toughness of about 5 MPa $(m)^{\frac{1}{2}}$.

It would be very desirable to have a silicon nitride ceramic of high fracture toughness and high fracture strength. Moreover, it would be highly desirable to have a process which would be reproducible, inexpensive, and amenable to industrial scale-up for preparing such a tough and strong silicon nitride ceramic.

US-A-4609633 discloses silicon nitride sintered bodies comprising:

(a) 0.5 to 25 weight percent of at least one oxide, nitride or oxynitride of a rare earth element selected from scandium, yttrium and the lanthanides;

(b) 0.2 to 30 weight percent of at least one oxide, nitride or oxynitride of a Group IIa element (viz. beryllium, magnesium, calcium, strontium, barium, and radium) or a nitride or oxynitride of a Group IIIb element (viz. boron, aluminum, gallium, indium, and thallium); and

(c) silicon nitride and inevitable impurities.

It is stated that the body cannot have combinations of a rare earth oxide (a) with a Group IIa oxide (b) (see column 2, lines 17/20) but it is apparent from the exemplified bodies (see Samples 1 to 4 and 15 to 18) that both a rare earth oxide (a) and a Group IIa oxide (b) can be present if a nitride or oxynitride (a) or (b) also is present. It is stated that the presence of the nitride or oxynitride in the sintering auxiliary heightens the bonding strength between second phases chiefly comprising the sintering auxiliary and the silicon nitride rigid phases after sintering and thereby prevents, inter alia, abnormal growth of silicon nitride grains (see column 2, lines 36/52). It is further stated that grains, as distinct from rods or needle-like structures, having a small aspect ratio provide excellent thermal shock resistance (see column 6, lines 40/50).

The composition of US-A-4609633 can additionally include one or more carbides or nitrides of a Group IVa, Va, or VIa element to enhance wear resistance and an oxide, nitride or oxynitride of a Group Ia element to enhance sinterability and densification. There is no exemplification of such compositions and, except for SiO_2, no information as to the content of said additional components.

WO-A-8907093 discloses a process for preparing a silicon nitride ceramic body, comprising preparing a powder mixture comprising

(a) silicon nitride in an amount sufficient to provide a ceramic body;

(b) a source of magnesium in an amount sufficient to promote densification of the powder;

(c) a source of yttrium in an amount sufficient to promote the essentially complete conversion of the starting silicon nitride to β-silicon nitride; and

(d) at least one whisker growth enhancing compound in an amount sufficient to promote the formation of β-silicon nitride whiskers, said compound being a derivative of an element selected from, inter alia, calcium, sodium, potassium, scandium, titanium, vanadium, chromium, manganese, iron, cobalt, nickel, copper, zinc, strontium, zirconium, niobium, barium, lanthanum, gallium, indium, hafnium, and tantalum.

and hot-pressing the powder mixture or greenware thereof under conditions such that densification and in situ formation of β-silicon nitride whiskers having an average aspect ratio of at least 2.5 occur and that said silicon nitride ceramic body is predominately β-silicon nitride.

The only exemplified sources of magnesium or yttrium in WO-A-8907093 are the oxides.

US-A-5021372 (published June 4th, 1991 in pursuance of US Patent Application No. 398801 filed August 25th, 1989 as a Continuation-in-part of US Patent Application No. 297627 filed January 13th, 1989, which was a Continuation-in-part of US Patent Application No. 148748 filed January 27th, 1988) discloses the preparation of self-reinforced silicon nitride ceramic bodies having a fracture toughness greater than 6 MPa $(m)^{\frac{1}{2}}$, and containing predominately β-silicon nitride whiskers having a high average aspect ratio by subjecting a powder mixture comprising:

(a) silicon nitride in an amount sufficient to provide a ceramic body;

(b) a densification aid, said densification aid being a non-oxide derivative of magnesium or a source of (i) a Group Ia element selected from lithium, sodium, potassium, rubidium, cesium, and francium; or (ii) a Group IIa element selected from beryllium, calcium, strontium, barium, and radium, said source being present in an amount sufficient to promote densification of the powder;

(c) a conversion aid, said conversion aid being a non-oxide derivative of yttrium or a source of (i) a Group IIIa element selected from scandium, actinium, and lanthanum; or (ii) a Group Ia element selected from lithium, sodium, potassium, rubidium, cesium and francium, said source being present in an amount sufficient to promote the essentially complete conversion of the starting silicon nitride to β-silicon nitride; and

(d) at least one whisker growth enhancing compound in an amount sufficient to promote the formation of β-silicon nitride whiskers, said compound being a non-oxide derivative of calcium, or a derivative of (i) a Group Ia element selected from sodium and potassium; (ii) copper; (iii) a Group IIa element selected from strontium and barium; (iv) zinc; (v) a Group IIIa element selected from scandium and lanthanum; (vi) a Group IVa element selected from titanium and zirconium; (vii) a Group Va element selected from vanadium and niobium; (viii) chromium; (ix) manganese; (x) a Group VIII element selected from iron, cobalt, and nickel; or mixtures thereof, or an oxide of a Group IIIb element selected from indium, gallium and boron; hafnium; or tantalum;

(b), (c) and (d) being derived from three different elements,

to conditions of temperature and pressure sufficient such that densification and in situ formation of β-silicon nitride whiskers having an average aspect ratio of at least 2.5 and such that the silicon nitride ceramic body has a fracture toughness greater than 6 MPa $(m)^{\frac{1}{2}}$ is formed.

It is stated in US-A-5021372 that the powder mixture can further comprises silica in an amount of from 2.3 to 6 weight percent based upon total weight of the powder mixture to improve fracture strength of resultant hot-pressed bodies. At the lower silica concentrations, it is present as impurity in commercially available silica nitride but at higher concentrations silica is added to the powder mixture.

EP-A-0471568 (published February 19th, 1992 and having a filing date of August 14th, 1991 and a priority date of August 15th, 1990) discloses the preparation of silicon nitride ceramic bodies having a fracture toughness greater than 6 MPa $(m)^{\frac{1}{2}}$ by subjecting a powder mixture comprising

(a) silicon nitride in an amount sufficient to provide a ceramic body;

(b) free silicon dioxide in an amount sufficient to promote densification of the powder, the sum of said amount and any silicon dioxide present in the silicon nitride being from 1 to 28 weight percent based on the total weight of the powder mixture;

(c) a conversion aid in an amount sufficient to attain essentially complete conversion of the starting silicon nitride to β-silicon nitride, said amount being from 0.2 to 29.5 weight percent based on the total weight of the powder mixture, the conversion aid being a source of (i) a Group IIIa element selected from yttrium, scandium, actinium, and lanthanum; or (ii) a Group Ia element selected from lithium, sodium, potassium, rubidium, cesium and francium, and

(d) at least one whisker growth enhancing compound in an amount sufficient to promote formation of β-silicon nitride whiskers, the amount being from 0.01 to 5 weight percent based upon total weight of the powder mixture, said compound being a source of (i) a Group Ia element selected from sodium and potassium; (ii) copper; (iii) a Group IIa element selected from calcium, strontium and barium; (iv) zinc; (v) a Group IIIa element selected from scandium and lanthanum; (vi) a Group IVa element selected from titanium and zirconium; (vii) a Group Va element selected from vanadium and niobium; (viii) chromium; (ix) manganese; (x) a Group VIII element selected from iron, cobalt, and nickel; or mixtures of two or more thereof, or an oxide of a Group IIIb element selected from indium, gallium and boron; hafnium; or tantalum,

(c) and (d) being derived from two different elements,

to conditions of temperature of at least 1750 °C and pressure of at least 3000 psig (20 MPa) sufficient to provide for densification of the powder mixture and in situ formation of β-silicon nitride whiskers having an average aspect ratio of at least 2.5 in an amount of at least 20 volume percent, as measured by viewing one plane of the silicon nitride ceramic body by scanning electron microscopy.

A first aspect of this invention is a process for preparing a self-reinforced silicon nitride ceramic body containing predominately β-silicon nitride whiskers having a high average aspect ratio. The process comprises subjecting a powder mixture comprising:

(a) silicon nitride in an amount sufficient to provide a ceramic body;

(b) a densification aid, said densification aid being a source of (i) a Group Ia element selected from lithium, sodium, potassium, rubidium, cesium, and francium; (ii) a Group IIa element selected from beryllium, magnesium, calcium, strontium, barium, and radium; (iii) zinc; (iv) a Group IIIb element

selected from indium and gallium; (v) silicon; (vi) a Group IVa element selected from hafnium and titanium; or (vii) tantalum, said source being present in an amount sufficient to promote densification of the powder;

(c) a conversion aid, said conversion aid being a source of (i) a Group IIIa element selected from scandium, yttrium, actinium, and lanthanum; or (ii) a Group Ia element selected from lithium, sodium, potassium, rubidium, cesium and francium, said source being present in an amount sufficient to promote the essentially complete conversion of the starting silicon nitride to β-silicon nitride; and

(d) at least one whisker growth enhancing compound in an amount sufficient to promote the formation of β-silicon nitride whiskers, said compound being a derivative of (i) a Group Ia element selected from sodium and potassium; (ii) copper; (iii) a Group IIa element selected from strontium, calcium and barium; (iv) zinc; (v) a Group IIIa element selected from scandium and lanthanum; (vi) a Group IVa element selected from titanium and zirconium; (vii) a Group Va element selected from vanadium and niobium; (viii) chromium; (ix) manganese; (x) a Group VIII element selected from iron, cobalt, and nickel; or mixtures thereof, or an oxide of a Group IIIb element selected from indium, gallium and boron; hafnium; or tantalum;

(b), (c) and (d) being derived from three different elements and provided that:

(1) when the powder mixture contains an oxide of a Group IIIa element, it does not also contain a nitride or oxynitride of a Group IIa or Group IIIb element;

(2) when the powder mixture contains a nitride or oxynitride of a Group IIIa element, it does not also contain an oxide, nitride or oxynitride of a Group IIa element or a nitride or oxynitride of a Group IIIb element;

(3) when the powder mixture contains a source of zinc, titanium, indium, gallium, hafnium or tantalum, it does not also contain free silicon dioxide; and

(4) when the powder mixture contains both a magnesium derivative as densification aid and a yttrium derivative as conversion aid, it contains also at least one preformed reinforcing material selected from β-silicon nitride in whisker or fiber form, and silicon carbide, titanium carbide, boron carbide, titanium diboride, aluminum oxide or zirconium oxide in whisker, fiber, particle or platelet form, in an amount sufficient to enhance the Palmqvist toughness of the ceramic body;

to conditions of temperature and pressure sufficient such that densification and in situ formation of β-silicon nitride whiskers having a high average aspect ratio occur. In this manner a self-reinforced silicon nitride ceramic body having a fracture toughness greater than 6 MPa $(m)^{\frac{1}{2}}$,as measured by the Chevron notch technique described hereinbelow, is formed.

For the purposes of the present invention a "high" average aspect ratio means an average aspect ratio of at least 2.5. The powder mixture optionally includes aluminum nitride or boron nitride in an amount of 0.01 to 5 weight percent, based upon total powder mixture weight. Any means may be used to apply pressure and temperature so long as sufficient densification and in situ whisker formation occur. Application of pressure and temperature beneficially occurs by hot-pressing or hot isostatic pressing, preferably by hot-pressing.

In a related aspect, the powder mixture further comprises a Palmqvist toughness enhancing amount of at least one preformed reinforcing material. The material is silicon carbide, titanium carbide, boron carbide, titanium diboride, aluminum oxide or zirconium oxide. The materials are present as whiskers, fibers, particles or platelets.

In a second aspect, this invention is a silicon nitride ceramic body having a fracture toughness greater than 6 MPa $(m)^{\frac{1}{2}}$, as measured by the Chevron notch technique described hereinbelow, comprising:

(a) a crystalline phase of β-silicon nitride of which at least 20 volume percent, as measured by viewing one plane of the silicon nitride ceramic body by scanning electron microscopy, is in the form of whiskers having an average aspect ratio of at least 2.5; and

(b) a glassy phase, in an amount not greater than 35 weight percent of the total weight, comprising a densification aid, a conversion aid, silica, and a beta-silicon nitride whisker growth enhancing compound.

The glassy phase optionally contains an amount, e.g., up to 15.0 percent by weight of the glassy phase, of aluminum nitride or boron nitride. The densification aid, the conversion aid and the whisker growth enhancing compound are the same as those detailed above in the first aspect. As in the first aspect, the densification aid, the conversion aid and the whisker growth enhancing compound are each based upon, or derived from, a different element and provided that:

(1) when the powder mixture contains an oxide of a Group IIIa element, it does not also contain a nitride or oxynitride of a Group IIa or Group IIIb element;

(2) when the powder mixture contains a nitride or oxynitride of a Group IIIa element, it does not also contain an oxide, nitride or oxynitride of a Group IIa element or a nitride or oxynitride of a Group IIIb

element;

(3) when the powder mixture contains a source of zinc, titanium, indium, gallium, hafnium or tantalum, it does not also contain free silicon dioxide; and

(4) when the powder mixture contains both a magnesium derivative as densification aid and a yttrium derivative as conversion aid, it contains also at least one preformed reinforcing material selected from β-silicon nitride in whisker or fiber form, and silicon carbide, titanium carbide, boron carbide, titanium diboride, aluminum oxide or zirconium oxide in whisker, fiber, particle or platelet form, in an amount sufficient to enhance the Palmqvist toughness of the ceramic body.

In a related aspect, the glassy phase further comprises a Palmqvist toughness enhancing amount of at least one preformed reinforcing material. The material is β-silicon nitride fibers or whiskers or silicon carbide, titanium carbide, boron carbide, titanium diboride, aluminum oxide or zirconium oxide in at least one form selected from whiskers, fibers, particles and platelets.

In a third aspect, this invention is a cutting tool comprising the above-identified silicon nitride ceramic body.

Unexpectedly, the silicon nitride ceramic body of this invention exhibits a significantly higher fracture toughness than the monolithic or whisker-reinforced silicon nitride ceramics of the prior art. Moreover, if the fracture toughness of the silicon nitride ceramic of this invention is normalized with respect to density, the normalized fracture toughness and fracture strength are among the highest known for any ceramic material.

Advantageously, the silicon nitride ceramic of this invention is self-reinforced. More advantageously, the process for preparing the novel, self-reinforced silicon nitride ceramic body of this invention is reproducible, amenable to industrial scale-up, and less expensive than processes using silicon carbide whisker reinforcement.

The silicon nitride starting material used in preparing ceramic body of this invention can be any silicon nitride powder, including the crystalline forms of α-silicon nitride and β-silicon nitride, or noncrystalline amorphous silicon nitride, or mixtures thereof. Preferably, the silicon nitride powder is predominately in the alpha crystalline form or the amorphous form, or mixtures thereof. More preferably, the starting silicon nitride is predominately in the alpha crystalline form. It is also advantageous if the preferred starting powder possesses a high α/β weight ratio. Preferably, the starting powder contains no greater than 20 weight percent β-silicon nitride; more preferably, no greater than 10 weight percent β-silicon nitride; most preferably, no greater than 6 weight percent β-silicon nitride.

Generally, the higher the purity of the starting silicon nitride powder, the better will be the properties of the finished ceramic body. Depending on the source, however, the silicon nitride powder may contain nonmetallic impurities. Some impurities may be tolerated in the powder, although it is preferred to minimize these as much as possible. Oxygen, for example, is present to some extent in the form of silica, SiO_2, which usually is found as a coating on the surface of the silicon nitride particles. The amount of silica varies according to the purity of the starting silicon nitride powder and its method of manufacture. The silica content may be reduced by leaching or increased by adding free silica in order to attain a desired total silica content. Preferably, the total silica content of the powder mixture is from 2.3 to 6 weight percent (based upon total weight of the powder mixture). In addition to oxygen, elemental silicon is usually present in amounts ranging up to 0.5 weight percent. These amounts of elemental silicon are not deleterious and can be tolerated. Other nonmetals, such as carbon which is likely to form silicon carbide during hot-pressing or sintering, are tolerable in small amounts.

The silicon nitride starting powder can be of any size or surface area provided that the ceramic body of this invention is obtained by hot-pressing. Large particles having an average diameter of 15 µm to 50 µm, for example, may be in the form of hard agglomerates which cannot be easily broken. Powders containing such agglomerates make poor ceramics. On the other hand, very fine powders having an average diameter less than 0.2 µm are difficult to obtain uniformly and to process. Preferably, the particles have an average diameter of 0.2 µm to 10.0 µm; more preferably, from 0.5 µm to 3.0 µm. Preferably, the surface area of the silicon nitride particles is 5 m^2/g to 15 m^2/g, as determined by the Brunauer-Emmett-Teller (BET) method of measuring surface area, which is described by C. N. Satterfield in *Heterogeneous Catalysis in Practice*, McGraw-Hill Book Company, 1980, pp. 102-105. More preferably, the surface area is 8 m^2/g to 15 m^2/g.

The silicon nitride is present in an amount which is suitably in a range of from 65 to 99.75 weight percent based on total powder mixture weight. The range is desirably from 80 to 97 weight percent based upon total powder mixture weight. When a reinforcing material is present, the amount of silicon nitride is reduced so that a total of silicon nitride plus reinforcing material falls within these ranges.

Raw silicon nitride powders cannot be densified to high densities in the absence of densification aids. Thus, at least one densification aid is admixed with the silicon nitride starting powder in a manner described hereinbelow for the purpose of promoting densification of the silicon nitride during processing. The

densification aids form a liquid phase into which the α-silicon nitride dissolves. The liquid phase forms at a temperature or over a temperature range which varies with the densification aid. The rate of mass transport of the α-silicon nitride is usually quite rapid in the liquid phase; thus, the silicon nitride density increases until a critical mass is reached and precipitation occurs.

US-A-4,883,776 teaches the use of magnesium oxide as a densification aid.

Any amount of a densification aid which promotes densification as described herein and produces the tough silicon nitride ceramic body of the invention is acceptable. The densification aid is beneficially a non-oxide derivative of magnesium, beryllium oxide, calcium oxide, strontium oxide, barium oxide or radium oxide. The densification aid is desirably calcium oxide or strontium oxide and is present in an amount of 0.04 to 27.0 weight percent based on the total weight of the powder mixture. The amount of densification aid is desirably 0.5 to 9.8 weight percent; and preferably, from 0.9 to 4.7 weight percent.

In addition to a densification aid, the powder mixture must contain a conversion aid. The conversion aid forms a glassy phase through which mass transport is, in general, considerably slower than in the densification aid. Thus, α-silicon nitride dissolves in the conversion aid on heating, but is not readily densified. Advantageously, however, the conversion aid promotes the rapid, essentially complete conversion of α-silicon nitride to β-silicon nitride. This conversion is most desirable because the β-silicon nitride in the form of elongate, single crystal whiskers or grains is responsible for the high fracture toughness and high fracture strength of the silicon nitride ceramic body of this invention. All references hereinafter to silicon nitride whiskers, single crystal whiskers and single crystal silicon nitride whiskers are intended to be synonymous and may be used interchangeably. Any amount of conversion aid can be employed in the starting powder providing the quantity is sufficient to cause the essentially complete conversion of the starting silicon nitride to β-silicon nitride, and is sufficient to produce the tough silicon nitride ceramic body of the invention. Preferably, the amount of conversion aid employed is 0.2 to 29.5 weight percent based on the total weight of the powder mixture. More preferably, the amount of conversion aid employed is 1.0 to 10.0 weight percent; most preferably, 1.7 to 8.5 weight percent.

The conversion aid is suitably a non-oxide derivative of yttrium or a source or derivative of an element selected from scandium, actinium, lanthanum, lithium, sodium, potassium, rubidium, cesium and francium. Non-oxide derivatives of yttrium include yttrium carbide. The conversion aid is beneficially scandium oxide, lanthanum oxide, actinium oxide or sodium oxide. The conversion aid preferably is lanthanum oxide or sodium oxide.

Surprisingly, the weight ratio of conversion aid to densification aid has been found to affect the fracture toughness of the finished ceramic, providing the whisker growth enhancing compound is also present in the powder mixture. Any weight ratio of conversion aid to densification aid is acceptable providing the fracture toughness shows an improvement over the fracture toughness value of 5 MPa $(m)^{\frac{1}{2}}$ for nonreinforced, monolithic silicon nitride. The weight ratio is suitably from 0.25 to 8. The weight ratio is beneficially 0.5 to 5; desirably, 1 to 3; and, preferably, 1 to 1.8. In the absence of a whisker growth enhancing compound, the conversion aid densification aid weight ratio has no significant effect on the fracture toughness.

The third component required to be present in the powder mixture is a whisker growth enhancing compound. This compound helps to provide a ceramic body of superior fracture toughness and high strength. Just how the whisker growth enhancing compound contributes to the excellent physical properties which are observed in the silicon nitride ceramic body of this invention is not completely understood. It is possible that the whisker growth enhancing compound improves the viscosity of the glassy phase thereby facilitating the nucleation of elongate whiskers or grains of β-silicon nitride; the latter being primarily responsible for the improved fracture toughness. The aforementioned theory is presented with the understanding that such a theory is not to be binding or limiting of the scope of the invention. Any amount of the compound in the starting powder is acceptable providing the amount is sufficient to promote the formation of β-silicon nitride whiskers, described hereinbelow, and sufficient to produce the tough silicon nitride ceramic body of this invention. Preferably, the amount of the compound employed is 0.01 to 5 weight percent based on the total weight of the powder mixture. More preferably, the amount of whisker growth enhancing compound employed is 0.1 to 1.0 weight percent; most preferably, from 0.2 to 0.5 weight percent.

In US-A-4,883,776, the presence of calcium, particularly calcium oxide, was found to provide advantages when silicon nitride powder compositions were formed by hot-pressing into finished ceramic bodies. Silicon nitride powders doped with up to 5.3 weight percent calcium oxide were found to be desirable. It was believed that commercial silicon nitride powders contained only 100 ppm or less of calcium oxide.

Acceptable results are believed to be attainable with derivatives of lithium, beryllium, magnesium, silicon, germanium, selenium, rubidium, molybdenum, technetium, ruthenium, rhodium, palladium, silver, cadmium, tin, antimony, tellurium, cesium, cerium, [illegible] promethium, samarium,

europium, gadolinium, terbium, dysprosium, holmium, erbium, thulium, ytterbium, lutetium, tungsten, rhenium, osmium, iridium, platinum, gold, thallium, lead, bismuth, polonium, francium, radium, thorium, protactinium, neptunium, americium, curium, berkelium, californium, einsteinium, fermium, mendelevium, nobelium, and lawrencium. Non-oxide derivatives of gallium, indium, hafnium, tantalum and boron may also produce satisfactory results. Skilled artisans recognize that elements 58 - 71 and 90 - 103 of the Periodic Table of the Elements, commonly referred to as "the Lanthanides", are not readily available in their pure form. They are, however, available as mixtures of two or more of such elements. Such mixtures are also believed to be suitable for purposes of the present invention. Skilled artisans also recognize that certain of the elements and their derivatives may be less desirable than the others based upon considerations such as availability and cost.

Suitable results are also obtained with non-oxide derivatives of calcium. Illustrative non-oxide derivatives include calcium boride, calcium carbide, calcium nitride and calcium disilicide.

Skilled artisans will recognize that results will vary depending upon both the element(s) of choice and the particular derivative(s) of that element or mixture of elements. The whisker growth enhancing aid is beneficially a source or derivative of niobium or an oxide of an element selected from potassium, sodium, strontium, barium, scandium, lanthanum, titanium, zirconium, vanadium, chromium, tungsten, manganese, iron, cobalt, nickel, copper, zinc, calcium, gallium, indium, hafnium, tantalum and boron. The whisker growth enhancing aid is desirably niobium stannate, niobium gallate, niobium boride, or an oxide of potassium, barium, scandium, niobium, titanium, chromium, tungsten, manganese, cobalt, nickel, zinc, calcium, gallium, indium, hafnium, tantalum. The whisker growth enhancing aid is preferably an oxide of an element selected from gallium, indium, hafnium, tantalum and boron.

It is desirable to use whisker growth enhancing compounds, densification aids and conversion aids in the form of powders which are pure and sufficiently small in size. Purity is not typically a problem, because commercially available materials used as whisker growth enhancing compounds, densification aids and conversion aids, particularly the oxide powders, generally contain less than 20 ppm each of assorted impurities. These levels of impurities are tolerable. Larger amounts of impurities, as for example in the 0.5 weight percent range, are not recommended as they may cause a change in the final ceramic composition and properties. A small powder particle size is favored, because dispersion is enhanced by smaller particles. Preferably, the oxide powders have an average particle size no greater than 5 μm in diameter.

Certain elements, e.g., sodium and potassium, may be used as a densification aid, a conversion aid or a whisker growth enhancing compound in a given powder mixture. No single element may, however, be used in an amount sufficient to function as two or more of these functions, e.g., as both a densification aid and a conversion aid.

It has now been found that incorporation into the powder mixture of a Palmqvist toughness enhancing amount of at least one preformed reinforcing material improves properties of the resultant silicon nitride body. Properties which are improved include room temperature toughness and high temperature strength and stiffness. The material is selected from β-silicon nitride fibers or whiskers or silicon carbide, titanium carbide, boron carbide, titanium diboride, aluminum oxide or zirconium oxide in at least one form selected from whiskers, fibers, particles and platelets.

The reinforcing material must be chemically compatible with the glassy phase and its components. Chemically compatible materials are selected from boron carbide, silicon carbide, titanium carbide, aluminum oxide, zirconium oxide and titanium diboride. Materials which are normally chemically incompatible with the glassy phase and its components may be rendered compatible by coating them with one of the aforementioned chemically compatible elements. Normally incompatible materials include aluminum nitride, magnesium oxide and mullite. Titanium carbide provides a satisfactory coating for the latter group of materials.

The reinforcing material must be present in an amount which is sufficient to enhance the Palmqvist toughness of the resultant silicon nitride body without substantially interfering with or eliminating the formation of elongate silicon nitride grains. The reinforcing material, when present, occupies space in the glassy phase in which elongate silicon nitride grains would otherwise grow in its absence. The amount of reinforcing material varies with the size of reinforcing material pieces, particles, fibers or whiskers as well as the volume occupied by the reinforcing material. Polycrystalline fibers provide acceptable results as a nominally continuous reinforcing material. Single crystal whiskers also provide acceptable results, albeit as a nominally discontinuous reinforcing material.

As a general rule, a given volume percentage of large particles, fibers, etc., will interfere less with formation of the elongate silicon nitride grains than an equal volume percentage of smaller particles, etc. Accordingly, satisfactory results are obtained with any of the following combinations of reinforcement material diameter and volume percentages, based upon glassy phase volume: (a) less than 0.2 μm

diameter, up to 10 volume percent; (b) from 0.2 µm to 0.5 µm diameter, up to 15 volume percent; (c) from 0.5 µm to 1.5 µm diameter, up to 25 volume percent; (d) from 1.5 µm to 2.5 µm diameter, up to 30 volume percent; (e) from 2.5 µm to 5.0 µm diameter, up to 35 volume percent; (f) from 5.0 µm to 15.0 µm diameter, up to 45 volume percent; (g) from 15.0 µm to 25.0 µm diameter, up to 50 volume percent; and (h) greater than 25.0 µm diameter, up to 65 volume percent. Irrespective of the reinforcing material diameter, the amount of reinforcing material, where used, is beneficially greater than 5 volume percent. The reinforcing materials have different densities. As such, a universal weight percentage is not applicable. The weight percentages corresponding to the foregoing volume percentages are readily determined given the density of a particular reinforcing material.

In the process of this invention, it is required to mix the starting silicon nitride powder, described hereinabove, with a combination of a densification aid, a conversion aid, a whisker growth enhancing compound and, optionally, a reinforcing material to obtain a powder mixture, which is used in preparing the tough silicon nitride ceramic body of this invention. The reinforcing material, when present, is beneficially added to the remaining components of the powder mixture after they are well mixed to minimize breakage or comminution of reinforcement material pieces. Suitable densification aids, conversion aids and whisker growth enhancing components are disclosed hereinabove. Ordinarily, the total quantity of the densification aid, conversion aid and the whisker growth enhancing compound is no greater than 35 weight percent of the total weight of the powder mixture. The 35 weight percent limit is also appropriate when a reinforcing material is used. The total quantity will depend, however, on probable end use applications for fired ceramics prepared from the powder mixture. For some applications, total quantities in excess of 35 weight percent will provide acceptable results. Preferably, however, the total quantity is 5 to 35 weight percent for medium temperature and/or the highest fracture toughness applications. By "medium temperature", it is meant temperatures from 900°C to 1200°C. Ceramic cutting tools are an example of a medium temperature and very high fracture toughness application. Preferably, the total quantity is 0.25 to 5 weight percent for high temperature and/or moderately high fracture toughness applications. By "high temperature", it is meant temperatures from 1200°C to 1400°C. Parts for ceramic engines are an example of a high temperature and moderately high fracture toughness application.

The preparation of the powder mixture containing silicon nitride, densification aid(s), conversion aid(s) and whisker growth enhancing compound(s), is accomplished in any suitable manner. Ball-milling of the components in powder form is one acceptable manner of preparation.

The preferred method of preparing the powder mixture comprises use of an attritor with zirconia balls to prepare a finely-divided suspension of silicon nitride and a powdered combination of the densification aid(s), the conversion aid(s) and the whisker growth enhancing compound(s) in a carrier medium, drying an admixture of the suspension and the attritor balls, beneficially after removing, by filtration or otherwise, excess carrier medium, and thereafter separating the attritor balls to obtain the powder mixture.

The preparation of the finely-divided suspension of silicon nitride and the combination of the densification aid(s), the conversion aid(s) and the whisker growth enhancing compound(s) in a carrier medium requires no particular order of addition of the components. For example, it is possible to add the powdered combination or powdered components thereof to a colloidal suspension of silicon nitride in a carrier medium or vice versa. Alternatively, all components of the powder mixture may be added simultaneously to the carrier medium prior to attritor milling. The latter method is preferred, particularly when an organic barrier medium such as toluene or an alcohol is employed.

The carrier medium may be any inorganic or organic compound which is a liquid at room temperature and atmospheric pressure. Examples of suitable carrier media include water; alcohols, such as methanol, ethanol and isopropanol; ketones, such as acetone and methyl ethyl ketone; aliphatic hydrocarbons, such as pentanes and hexanes: and aromatic hydrocarbons, such as benzene and toluene. The carrier medium is desirably an organic liquid, preferably toluene or an alcohol such as methanol. The function of the carrier medium is to impart a viscosity suitable for mixing to the solid powders. Any quantity of carrier medium which achieves this purpose is sufficient and acceptable. Preferably, a quantity of carrier medium is employed such that the solids content is 20 volume percent to 50 volume percent. More preferably, a quantity of carrier medium is employed such that the solids content is 35 volume percent to 45 volume percent. Below the preferred lower limit the viscosity of the solid suspension may be too low and the deagglomeration mixing may be ineffective. Above the preferred upper limit the viscosity may be too high, and the deagglomeration mixing may be difficult.

The components of the powdered combination are added to the carrier medium in any manner which gives rise to a finely dispersed suspension of the components. Typically, the process is conducted in a large vessel at room temperature (taken as 23°C) under air with vigorous stirring. Any common stirring means is suitable, such as a ball-milling [illegible] An ultrasonic vibrator may be [illegible]

supplementary manner to break down smaller agglomerates. The attrition mixer is preferred.

To aid in the dispersion of components of the powder mixture, optionally one or more surfactants or dispersants can be added to the suspension. The choice of surfactant(s) or dispersant(s) can vary widely as is well-known in the art.

If the carrier medium is toluene, a coupling agent, such as an aluminate coupling agent commercially available from Kenrich Petrochemicals under the trade designation KEN-REACT KA 322, may be used to aid in forming a suspension. When using an alcohol such as methanol, a dispersant such as a polyethyleneimine may be used to facilitate mixing and a flocculant such as oleic acid may be used to ease recovery of the powder mixture.

Any amount of surfactant or dispersant is acceptable providing dispersion of powder mixture components is improved. Typically, the amount of surfactant is 0.01 to 1.0 weight percent of the powder mixture.

The finely-divided suspension is now ready for processing into greenware. For example, the suspension can be slip-cast by techniques well-known in the art for eventual sintering. Alternatively, the suspension can be dried into a powder and ground for use in hot-pressing processes. Drying is accomplished by standard drying means, such as by spray-drying or oven drying under a nitrogen purge. Preferably, drying of the admixture of the powder mixture and the attritor balls is accomplished in an oven under a nitrogen purge after removal of excess carrier medium. During the drying process, additional free carrier medium is removed. The temperature of the drying depends on the boiling point of the carrier medium employed. Typically, the drying process is conducted at a temperature just below the boiling point of the carrier medium under atmospheric pressure. Preferably, the carrier medium is toluene or an alcohol and the temperature of drying is 50 °C. After drying, the resulting powder is separated from the attritor balls and sieved through a screen to obtain a powder having a maximum agglomerate diameter of 100 µm. The screen size is usually less than 60 mesh (250 µm); more preferably, less than 80 mesh (180 µm). The powder which is obtained on sieving is the powder mixture which is used in the hot-pressing process of this invention.

When reinforcing materials are included in the powder mixture, the foregoing procedure is modified depending upon the form of the reinforcing material. If the reinforcing material is in a form other than long or continuous fibers, the reinforcing material is added to the finely dispersed suspension of components and mixed or attrited for a suitable length of time. Attrition time largely depends upon a balancing of the extent of reinforcing material agglomeration with its friability or fragility. In other words, attrition time is long enough to break up most, if not all, of the agglomerates. It is also short enough to maintain sufficient reinforcing material integrity to provide a desired degree of reinforcement. The additional attrition time will also depend upon the reinforcing material. A typical time need to accomplish dispersion of the reinforcing material will vary from 10 minutes to 45 minutes. The time is beneficially from 10 to 20 minutes. If the reinforcing material is in the form of fibers, also known as continuous fibers, no additional attrition time is required. The fibers are suitably immersed in the finely dispersed suspension to deposit a coating of the suspension on their outer surface. The fibers are then removed from the suspension and dried before further processing. If desired, multiple coatings may be applied in this manner. The dried, coated fibers, whether in the form of single fibers or a fiber mat or fabric, are beneficially surrounded by the powder mixture in a hot-pressing die and then hot-pressed as described herein. Other known methods of processing fibers may also be used.

The preferred method of processing the powder mixture is by hot-pressing, which comprises heating the powder under pressure to obtain the densified ceramic body. Any standard hot-pressing equipment is acceptable, such as a graphite die equipped with a heating means and a hydraulic press. Particularly suitable results are obtained when the die is fabricated from a material which is substantially non-reactive with components of the powder mixture at hot-pressing temperatures and has a mean linear coefficient of expansion greater than silicon nitride. The use of such a die material aids in the preparation of near net shapes without post-densification machining operations. The die material is desirably titanium carbide. R. Morrell, Handbook of Properties of Technical and Engineering Ceramics, pages 82-83 (1985), lists the mean linear coefficients respectively for silicon nitride and titanium carbide as 3.6×10^{-6} K^{-1} and 8.2×10^{-6} K^{-1}. The hot-pressing is conducted under an inert atmosphere, such as nitrogen, to prevent the oxidation and decomposition of silicon nitride at high temperatures. The direction of pressing is uniaxial and perpendicular to the plane of the die plates.

Any processing temperature and pressure will suffice providing the novel silicon nitride ceramic of this invention, described hereinbelow, is obtained. Typically, however, the temperature must be carefully controlled, because the elongate β-silicon nitride whiskers are found to form in a narrow temperature range. Preferably, the temperature is maintained during pressurizing from 1750 °C to 1870 °C. More preferably the temperature is maintained from 1800 °C to 1850 °C. Most preferably, the temperature is maintained from

1820 °C to 1840 °C. Below the preferred lower temperature limit the formation of elongate β-silicon nitride whiskers may be retarded. Above the preferred upper temperature limit the silicon nitride may decompose, and special pressure equipment may be required to conduct the densification. In the absence of a reinforcing material, the use of high pressure techniques such as hot isostatic pressing may allow use of higher temperatures, e.g. up to 2000 °C or even 2100 °C. It is noted that the accurate measurement of high temperatures, such as those quoted hereinabove, is technically difficult. Some variation in the preferred temperature range may be observed depending on the method employed in measuring the temperature. The preferred temperatures of this invention are measured by use of a tungsten-rhenium thermocouple, obtained from and calibrated by the Omega Company.

While the pressure during hot-pressing is important, it is not quite as critical a parameter as temperature. Typically, the pressure should be sufficient to cause densification of the green body. Preferably, the pressure is 3000 psig (20.8 MPa) to 6000 psig (41.5 MPa); more preferably, from 4000 psig (27.7 MPa) to 5500 psig (38.0 MPa); most preferably, 4500 psig (31.1 MPa) to 5200 psig (36.0 MPa). Below the preferred lower pressure limit the powder will not be sufficiently densified. Above the preferred upper pressure limit the powder will densify in a shorter time and at a lower temperature. Although less rigorous processing conditions seem on the surface to be desirable, the formation of elongate β-silicon nitride crystals may be inhibited at lower temperatures and shorter pressing times.

The amount of time that the powder mixture is heated under pressure should be sufficient to bring the powder to essentially complete densification. Generally, ram movement is a good indicator of the extent of densification. As long as the ram continues to move, the densification is incomplete. When the ram has stopped moving for at least 15 minutes, the densification is essentially complete at 99 percent or greater of the theoretical value. Thus, the time required for hotpressing is the time during ram movement plus an additional 15 to 30 minutes. Preferably, the time is 15 minutes to 2 hours; more preferably, from 30 minutes to 90 minutes; most preferably, 45 minutes to 75 minutes.

The hot-pressing method of densification, described hereinbefore, allows for the formation of silicon nitride ceramic articles which can be used as cutting tools. A variety of shapes can be made by hot-pressing, one common shape being a flat plate. These plates may range in size from 2 inches (5 cm) in length by 1.5 inches (3.8 cm) in width by 0.45 inch (1.14 cm) in thickness to 16 inches (40.6 cm) in length by 16 inches (40.6 cm) in width by 1.0 inch (2.5 cm) in thickness. Smaller and larger plates can also be fabricated, as determined by the size of the hot-pressing plaques. Cutting tools can be fabricated by slicing and grinding these plates into a variety of cutting tool shapes.

The silicon nitride ceramic body which is produced by the hot-pressing process of this invention is a dense material having no significant porosity. Preferably, densification proceeds to greater than 95 percent of the theoretical value; more preferably, to greater than 97 percent of the theoretical value; most preferably, to greater than 99 percent of the theoretical value. Moreover, as measured by X-ray diffraction, the silicon nitride is present in the β-crystalline form, indicating essentially complete alpha to beta conversion during processing. Quite unexpectedly, the β-silicon nitride is present predominately as single crystal, "needle-like" whiskers or elongate grains, as determined by both scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The size of the hexagonal β-silicon nitride grains is usually 1 µm to 20 µm in length with a mean diameter of from 0.2 µm to 1.5 µm; preferably from 3 µm to 10 µm in length with a mean diameter from 0.3 µm to 1.0 µm.

Since the whiskers are oriented randomly, it is difficult to determine exactly the percentage of silicon nitride which exists as whiskers, as opposed to equiaxed particles. The measurement is made by viewing one plane of the silicon nitride ceramic in a scanning electron microscope (SEM) and measuring the percentage by volume occupied by whiskers having an aspect ratio between 2 and 16. It is observed that the whiskers are homogeneously distributed and randomly oriented throughout the ceramic body, and that the volume occupied by the whiskers is approximately the same in all planes. Typically, the percentage of silicon nitride whiskers having an aspect ratio of between 2 and 16 is at least 20 volume percent as measured in a plane. Preferably, the percentage of silicon nitride whiskers having an aspect ratio between 2 and 16 is at least 35 volume percent as measured in a plane. Unexpectedly, the whiskers are found to have a high average aspect ratio. Typically, the average aspect ratio of the silicon nitride whiskers is at least 2.5; preferably, at least 5.5. It is noted that because the aspect ratio is measured in a plane, the average aspect ratio is a lower bound. For example, a whisker which is perpendicular to the plane may have an apparent aspect ratio of less than 2; whereas the true aspect ratio may be very much greater than 2.

In addition to the β-silicon nitride phase the ceramic body of this invention contains a glassy second phase, which constitutes no greater than 35 weight percent of the total weight. The glassy second phase has a bulk chemical composition consisting essentially of from 8 to 60 weight percent of a densification aid from 15 to 64 weight percent of a [illegible] 77 weight percent silica, and [illegible]

weight percent of at least one whisker growth enhancing compound, as determined by neutron activation analysis; and wherein the conversion aid to densification aid weight ratio is 0.25 to 8.

Small quantities of other phases may be present in a total amount not exceeding 10 weight percent. One of the phases, enstatite, possesses a fiber-like, layered and ordered structure. The typical size of the particles of this phase is 500 nanometers (nm) in width by 0.7 μm to 1.0 μm in length. This phase, being distributed throughout the glassy phase, connects and bridges Si_3N_4 whiskers. In other words, unique microstructures can be created with small needles or fibers of enstatite situated between comparatively large Si_3N_4 whiskers or particles.

The mechanical properties of the self-reinforced silicon nitride ceramic body are readily measured by use of standard tests. In particular, fracture toughness (K_{IC}) is measured according to the Chevron notch and the Palmqvist methods described hereinafter. Fracture strength (modulus of rupture) is measured according to the Military Standard 1942b test. Hardness is measured according to the Vickers indentation test.

Fracture strength (modulus of rupture) measures the resistance of the material to fracture under a steady load. Fracture strength is defined as the maximum unit stress which the material will develop before fracture occurs. Test bars are prepared by cutting rectangular bars (45 mm x 4 mm x 3 mm) of the silicon nitride ceramic in a plane perpendicular to the pressing direction. The bars are ground on the surfaces parallel to the pressing plates using a 500 grit grinding wheel (Military Standard 1974). The fracture strength is measured at room temperature using a 4-point bend test with 20 mm span and crosshead speed of 0.5 mm/min. Typically, the fracture strength at room temperature is at least 650 MPa. Preferably, the fracture strength at room temperature ranges from 825 MPa to 1250 MPa; more preferably, from 1000 MPa to 1150 MPa. High temperature strength is measured using a 3-point bend test with 20 mm span and crosshead speed of 0.5 mm/min. Typically, at 1000 °C the fracture strength is at least 550 MPa. Typically, at 1300 °C the fracture strength is at least 300 MPa.

Toughness measures the resistance of the material to fracture under a dynamic load. More specifically, fracture toughness is defined as the maximum amount of energy which a unit volume of material will absorb without fracture. In the present invention two methods are employed to measure fracture toughness. The first of these is the Chevron notch test. Test bars are prepared as described hereinabove, and additionally scored with a Chevron notch. The test bars are then subjected to a 3-point bend test with 40 mm span and crosshead speed of 0.5 mm/min. Typically, the fracture toughness of the silicon nitride ceramic body of this invention, as measured at room temperature (taken as 23 °C) by the Chevron notch technique, is greater than 6 MPa $(m)^{1/2}$. Preferably, the room temperature fracture toughness is greater than 7 MPa $(m)^{1/2}$; more preferably, greater than 8 MPa $(m)^{1/2}$. Most preferably, the room temperature fracture toughness ranges from 9 MPa $(m)^{1/2}$ to 14 MPa $(m)^{1/2}$. Preferably, at 1000 °C the fracture toughness is greater than 6 MPa $(m)^{1/2}$. More preferably, at 1000 °C the fracture toughness ranges from 7 MPa $(m)^{1/2}$ to 12 MPa $(m)^{1/2}$.

In the evaluation of cutting tool materials it is useful to measure the Palmqvist toughness and the Vickers hardness. Both measurements can be made simultaneously on one test sample, and therefore these tests are very convenient.

The Vickers hardness test measures the resistance of the ceramic material to indentation. A sample, approximately 1 cm in length by 1 cm in width by 1 cm in height, is placed on a flat surface, and indented with a standard Vickers diamond indentor at a crosshead speed of 0.02 in/min (0.05 cm/min). The Vickers hardness number is calculated from the applied load, in this case 14 kg, and the cross-sectional area of the indentation. Prior to making the test, the test sample is polished in a special manner. First, the sample is cleaned and rough spots are flattened by use of a 220-grid diamond wheel. Next, a 45 μm diamond wheel is used to start the polishing. Next, the sample is treated to a series of polishings at 30 psi (200 kPa) and 200 rpm in the following consecutive manner: three five-minute intervals with 30 μm diamond paste, three five-minute intervals with 15 μm diamond paste, three five-minute intervals with 6 μm diamond paste, two five-minute intervals with 1 μm diamond paste, and one five-minute interval with 0.25 μm diamond paste. Between each interval the sample is thoroughly cleansed by washing with water and sonicating for two minutes. The Vickers hardness number of the silicon nitride ceramic of this invention is at least 1325 kg/mm^2 at room temperature. Preferably, the Vickers hardness number ranges from 1340 kg/mm^2 to 1600 kg/mm^2 at room temperature; more preferably, from 1450 kg/mm^2 to 1600 kg/mm^2.

The Palmqvist toughness test is an extension of the Vickers test. (See S. Palmqvist in Jerndontorets Annalen, 141 (1957), 300, for a description of the Palmqvist toughness test.) The test sample is prepared and indented as in the Vickers test, but the 14-kg load is additionally held for 15 seconds. The sample cracks. The measurements of the indented diagonals and the crack lengths are made on a Nikon UM2 microscope at 1000x magnification. The Palmqvist toughness (W) is directly proportional to the applied load (P) and inversely proportional to the crack length (L). Preferably, the silicon nitride ceramic body of this

invention exhibits a Palmqvist toughness at room temperature of at least 37 kg/mm. Preferably, the silicon nitride ceramic body of this invention exhibits a Palmqvist toughness at room temperature from 37 kg/mm to 52 kg/mm; more preferably, from 45 kg/mm to 52 kg/mm.

The following examples serve to illustrate the novel self-reinforced silicon nitride composition of this invention, the method of preparing the novel silicon nitride ceramic, and the utility of the composition as a cutting tool. The examples are not intended to be limiting of the scope of this invention. All percentages are weight percent unless otherwise noted.

Examples 1(a-b)

Using the procedure of Example 5 of WO-A-8907093, two hot-pressed silicon nitride ceramic bodies are prepared by substituting equal weight percentages of strontium oxide (SrO) (Example 1a) or calcium oxide (CaO) (Example 1b) for the magnesium oxide (MgO) used in said Example 5. Physical property data for the two bodies and for Examples 5c and 5s of WO-A-8907093 are summarized in Table I. CaO is the whisker growth enhancing compound for Examples 1a and 5s. SrO is the whisker growth enhancing compound for Examples 1b and 5c.

TABLE I

Example No.	Fracture Strength (MPa)	Fracture Toughness ($MPa \cdot m^{\frac{1}{2}}$)	Vickers Hardness (kg/m^2)
1a	1027	6.67	1634
5s	896	9.5	1430
1b	1014	6.61	1556
5c	869	8.56	1604

The data presented in Table I demonstrate that strontium oxide and calcium oxide are suitable substitutes for magnesium oxide. Similar results are expected with other oxides from Group IIa of the Periodic Table of the Elements, namely beryllium oxide, barium oxide and radium oxide.

Example 2

Using the procedure of Example 1 and the composition of Example 1b, save for the substitution of 0.5 weight percent MgO for a like amount of SrO, a hot-pressed silicon nitride ceramic body is prepared. Physical property data for the body are as follows:
Fracture Strength (MPa) - 800
Fracture Toughness ($MPa \cdot m^{\frac{1}{2}}$) - 7.94
Vickers Hardness (kg/m^2) - 1545
The data demonstrate the suitability of MgO as a whisker growth enhancing compound.

Example 3.

Using the procedure of Example 6 of WO-A-8907093, two hot-pressed silicon nitride ceramic bodies are prepared from the compositions shown in Table IIA. Physical property data for the bodies are shown in Table IIB.

TABLE IIA

Example No.	Si_3N_4	Y_2O_3	SrO	AlN	TiO_2
3a	96	2.32	1.28	0.27	0.13
3b	97	1.74	0.96	0.2	0.1

TABLE IIB

Example No.	Fracture Strength (MPa)	Fracture Toughness ($MPa \cdot m^{\frac{1}{2}}$)	Vickers Hardness (Kg/mm^2)
3a	820	8.52	1650
3b	770	8.29	1640

The data shown in Table IIB demonstrate the suitability of SrO as a substitute for MgO in the preparation of self-reinforced silicon nitride bodies. Similar results are expected with other oxides from Group IIA of the Periodic Table of the Elements.

Evaluation of Cutting Tool Effectiveness

The hot-pressed silicon nitride body of Example 3b is diamond ground according to American National Standards Institute (A.N.S.I.) standards into an SNG 434 style cutting tool insert. The cutting edge is chamfered at a 30° angle with a 0.006 inch (0.015 cm) width.

The insert is tested in a face milling application using a 40 Horsepower Cincinnati #5 single spindle, knee and saddle, vertical milling machine with a 5 Horsepower (3.7 Kw) variable speed table. The work material is Class 30 grey cast iron, four inches (10.16 cm) wide and 12 inches (30.48 cm) long with a measured hardness of 170 BHN (220 kg/mm^2). A milling cutter having a 12 inch (30.48 cm) diameter, one tooth milling cutter, is used with a -5° axial rake and a -5° radial rake. A 15° lead angle is employed. The machine is run at a cutting speed of 3000 surface feet per minute (914 meters per minute), a 0.060 inch (0.152 cm) depth of cut, and a feed rate of 0.013 inch (0.330 mm) per revolution (or tooth). The center line of the cutter and the center line of the workpiece are coincident. No cutting fluid is used.

Successive passes are taken on the cast iron work material. The cutting edge is examined for flank wear and chippage after each pass. Testing is terminated when the flank wear or the chippage exceeds 0.010 inch (0.025 cm) in depth as measured with a 30-power microscope. The insert removes 590 cubic inches (9668 cm^3) of iron prior to failure. An SNG 434 style cutting tool insert prepared from a nominal silicon nitride material (actually a silicon-alumina-nitride or sialon) marketed by Kennametal Corporation under the trade designation Kyon™ 3000 removes 340 cubic inches (5572 cm^3) of iron prior to failure. An SNG 434 style cutting tool insert prepared from a silicon nitride material marketed by Boride Products under the trade designation US-20 removes 311 cubic inches (5096 cm^3) of iron prior to failure.

The foregoing illustration demonstrates the suitability of the self-reinforced silicon nitride material prepared in Example 3b in cutting tool applications. Similar results are expected with other compositions disclosed herein.

Example 4

Using the procedure of Example 5 of WO-A-8907093, and a composition identical to that of said Example 5s, save for the substitution of lanthanum oxide for yttrium oxide, a hot-pressed silicon nitride body is prepared. Physical property data for the body are as follows:

Fracture Strength (MPa) - 930

Fracture Toughness ($MPa \cdot m^{\frac{1}{2}}$) - 9.0

Vickers Hardness (kg/m^2) - 1526

The data demonstrate the suitability of lanthanum oxide as a conversion aid. Similar results are expected with other oxides of elements from Group IIIA of the Periodic Table of the Elements. Satisfactory results are also expected with non-oxide sources of the Group IIIA elements as well as sources of Group IIA elements.

Example 5

Using the procedure of Example 5 of WO-A-8907093, and a composition identical to that of said Example 5s, save for the substitution of sodium oxide for yttrium oxide in present Example 5a and the substitution of sodium oxide for magnesium oxide in present Example 5b, two hot-pressed silicon nitride bodies are prepared. Physical property data for the bodies are shown in Table III.

TABLE III

Example No.	Fracture Strength (MPa)	Fracture Toughness (MPa•m^{½})
5a	925	8.54
5b	720	7.4

The data presented in Table III demonstrate that sodium oxide is an effective substitute either as a densification aid (Example 5b) or a conversion aid (Example 5a). Similar results are obtained by substituting zinc oxide (ZnO), hafnium oxide (HfO) and tantalum oxide ($Ta2O_5$) for magnesium oxide. Similar results are expected with other sources of sodium as well as sources of other elements of Group IA of the Periodic Table of the Elements.

Example 6

Dense pieces of a number of different ceramic materials are polished and placed into the cavity of a graphite die similar to that of Example 1 of WO-A-8907093. The ceramic materials are titanium carbide, boron carbide, silicon carbide, aluminum oxide, zirconium oxide, magnesium oxide, aluminum nitride, titanium diboride and mullite. A powder mixture, prepared as in said Example 1, is poured into the die cavity and hot-pressed as in said Example 1 save for increasing the hot-pressing temperature to 1850 °C and the time at pressure to one hour. The powder mixture contains 90 percent silicon nitride, 5.8 percent yttria, 3.2 percent magnesia, 0.3$\dot{3}$ percent calcia and 0.67 percent silica.

The hot-pressed material is sectioned to provide interfaces between the silicon nitride composition and each of the previously densified ceramic materials. The interfaces are polished and examined by scanning electron microscopy (SEM) for the presence of elongated grains of β-silicon nitride. The SEM examination shows that elongated grains of β-silicon nitride are found at or near the interfaces of all previously densified ceramic materials save for aluminum nitride, magnesia and mullite. Based upon this preliminary examination, the latter three materials are believed to be unsuitable for use as reinforcing materials in preparing the silicon nitride ceramic bodies of the present invention. Similar results are attainable with other forms of the ceramic materials evaluated in this example.

Example 7

The powder mixture of Example 6 is admixed with varying amounts of silicon carbide whiskers (American Matrix) and hot-pressed as in Example 6. The whiskers have a number average diameter of 0.9 micrometer and an average aspect ratio of 11. The resultant hot-pressed bodies are tested for Vickers hardness and Palmqvist toughness as in Example 1 of WO-A-8907093. The amounts of silicon carbide whiskers and the test results are shown in Table IV.

TABLE IV

Sample Number	Volume Percent SiC Whiskers	Vickers Hardness (kg/mm^2)	Palmqvist Toughness (kg/mm)
7a	10	1580	44.3
7b	20	1587	37.2
7c	25	1587	37.0
7d	30	1595	36.1

The data presented in Table VI show that SiC whisker loadings of 30 volume percent provide a Palmqvist Toughness which approaches the values of 30 to 36 kg/mm reported for hot-pressed silicon nitride having neither elongate silicon nitride grains nor reinforcing materials such as silicon carbide whiskers admixed therewith. All of the samples in Table VI, when examined by SEM as in Example 19, show the presence of elongated silicon nitride grains. By way of contrast, hot-pressed bodies having SiC whisker loadings in excess [illegible] [illegible]tain no elongate silicon nitride [illegible] Simila[illegible]

are obtained with other reinforcing materials and compositions all of which are disclosed herein.

Example 8

A powder mixture containing 98 percent silicon nitride, 0.74 percent yttria, 0.7 percent silica, 0.46 percent magnesia and 0.1 percent tantalum oxide is prepared as in Example 1 of WO-A-8907093. A portion of the powder mixture is mixed with an amount of the same silicon carbide whiskers as in Example 20 to provide an admixture containing 25 weight percent silicon carbide whiskers. Equal volumes of the powder mixture and the admixture are converted to hot-pressed silicon nitride bodies using the procedure of Example 7. The resultant bodies are subjected to Vickers Hardness (VH) (kg/mm^2) and Fracture Strength (FS) (MPa) testing as in said Example 1. The bodies are also tested for Young's Modulus (YM) (GPa) in accordance with Military Standard 1942b at elevated temperatures. The test results are shown in Table V.

TABLE V

Sample No.	SiC Whiskers	20 °C		1200 °C		1375 °C	
		VH	FS	FS	YM	FS	YM
8a	yes	1810	730	475	278	285	71
8b	no	1614	792	543	200	206	22

The data presented in Table V demonstrate that the presence of a reinforcing material in addition to the elongate silicon nitride grains grown in situ provides improvements in high temperature strength, e.g., at 1375 °C, and Young's Modulus, e.g., at temperatures of 1200 °C or above. The data also show that hardness at room temperature (20 °C) is improved by the addition of such a reinforcing material. Similar results are obtained with other reinforcing materials and compositions all of which are disclosed herein.

Example 9

A powder mixture containing 71.69 percent silicon nitride, 4.6 percent yttria, 2.54 percent magnesia, 1.09 percent silica, 0.4 percent zirconia, and 19.68 percent silicon carbide platelets (C-Axis Corp.) is prepared as in Example 1 of WO-A-8907093 save for adding the platelets after the other components are well dispersed. Prior to adding the platelets, a portion of the mixture is removed from the mixing apparatus and recovered as in said Example 1. Mixing is continued for the remainder of the mixture for a period of ten minutes to provide an admixture which is recovered as in said Example 1. The platelets have an aspect ratio of 8 to 10 and an average diameter of 24µm. Equal volumes of the powder mixture and the admixture are converted to hot-pressed silicon nitride bodies using the procedure of Example 7. The resultant bodies are subjected to Vickers Hardness (VH) (kg/mm^2) and Palmqvist Toughness (kg/mm) testing. Test results are shown in Table VI.

TABLE VI

Sample Number	SiC Platelets	Vickers Hardness (kg/mm^2)	Palmqvist Toughness (kg/mm)
9a	yes	1542	49.4
9b	no	1525	45.1

The data presented in Table VI show that platelets, like whiskers, provide satisfactory results when used as reinforcing media in conjunction with elongate silicon nitride grains found in silicon nitride bodies of the present invention. Similar results are obtained with other reinforcing materials and compositions all of which are disclosed herein.

Example 10

Example 9 is replicated save for changes in the type of reinforcing media, the amount of reinforcing media or both. The reinforcing media are the platelets of Example 9, the whiskers of [illegible]

average diameter silicon carbide whiskers (Tateho Chemical Industries Co., Ltd.). The resultant silicon nitride bodies are subjected to Palmqvist Toughness (kg/mm) testing. Test results are shown in Table VII together with the average diameter and weight percent of reinforcing media.

TABLE VII

Sample No.	SiC		Palmqvist Toughness (kg/mm)
Sample No.	Diameter (μm)	Amount (%)	
10a	.25	10	37.4
10b	.25	20	35.7
10c	0.9	20	37.2
10d	0.9	30	36.1
10e	24.0	20	49.4
10f	24.0	40	37.3

The results shown in Table VII demonstrate that reinforcing media size plays an important part in determining the amount of reinforcing media which is suitable for a given composition. Similar results are obtained with other reinforcing materials and compositions all of which are disclosed herein.

Claims

1. A process for preparing self-reinforced silicon nitride ceramic body having a fracture toughness greater than 6 MPa $(m)^{\frac{1}{2}}$, and containing predominately β-silicon nitride whiskers having a high average aspect ratio. The process comprises subjecting a powder mixture comprising:
   (a) silicon nitride in an amount sufficient to provide a ceramic body;
   (b) a densification aid, said densification aid being a source of (i) a Group Ia element selected from lithium, sodium, potassium, rubidium, cesium, and francium; (ii) a Group IIa element selected from beryllium, magnesium, calcium, strontium, barium, and radium; (iii) zinc; (iv) a Group IIIb element selected from indium and gallium; (v) silicon; (vi) a Group IVa element selected from hafnium and titanium; or (vii) tantalum, said source being present in an amount sufficient to promote densification of the powder;
   (c) a conversion aid, said conversion aid being a source of (i) a Group IIIa element selected from scandium, yttrium, actinium, and lanthanum; or (ii) a Group Ia element selected from lithium, sodium, potassium, rubidium, cesium and francium, said source being present in an amount sufficient to promote the essentially complete conversion of the starting silicon nitride to β-silicon nitride; and
   (d) at least one whisker growth enhancing compound in an amount sufficient to promote the formation of β-silicon nitride whiskers, said compound being a derivative of (i) a Group Ia element selected from sodium and potassium; (ii) copper; (iii) a Group IIa element selected from strontium, calcium and barium; (iv) zinc; (v) a Group IIIa element selected from scandium and lanthanum; (vi) a Group IVa element selected from titanium and zirconium; (vii) a Group Va element selected from vanadium and niobium; (viii) chromium; (ix) manganese; (x) a Group VIII element selected from iron, cobalt, and nickel; or mixtures of two or more thereof, or an oxide of a Group IIIb element selected from indium, gallium and boron; hafnium; or tantalum;

   (b), (c) and (d) being derived from three different elements and provided that:
   (1) when the powder mixture contains an oxide of a Group IIIa element, it does not also contain a nitride or oxynitride of a Group IIa or Group IIIb element;
   (2) when the powder mixture contains a nitride or oxynitride of a Group IIIa element, it does not also contain an oxide, nitride or oxynitride of a Group IIa element or a nitride or oxynitride of a Group IIIb element;
   (3) when the powder mixture contains a source of zinc, titanium, indium, gallium, hafnium or tantalum, it does not also contain free silicon dioxide: and
   (4) when the powder mixture contains both a magnesium derivative as densification aid and a yttrium derivative as conversion aid, it contains also at least one preformed reinforcing material selected from β-silicon nitride in whisker [illegible] con carbide, titanium carbide [illegible] carbide.

titanium diboride, aluminum oxide or zirconium oxide in whisker, fiber, particle or platelet form, in an amount sufficient to enhance the Palmqvist toughness of the ceramic body;
to conditions of temperature and pressure sufficient such that densification and in situ formation of β-silicon nitride whiskers having an average aspect ratio of at least 2.5 and such that the silicon nitride ceramic body has a fracture toughness greater than 6 MPa $(m)^{\frac{1}{2}}$ is formed

2. The process of Claim 1 wherein the β-silicon nitride whiskers have an aspect ratio of 2 to 16 and are present in an amount of at least 20 volume percent, as measured by viewing one plane of the silicon nitride ceramic body by scanning electron micrography.

3. The process of Claim 1 or Claim 2 wherein the starting silicon nitride contains no greater than 10 weight percent β-silicon nitride.

4. The process of any one of the preceding Claims wherein the densification aid is present in an amount of 0.05 to 27.0 weight percent based on the total weight of the powder mixture.

5. The process of any one of the preceding Claims wherein the densification aid is selected from oxides of strontium, calcium or sodium.

6. The process of any one of the preceding Claims wherein the conversion aid is present in an amount of from 0.2 to 29.5 weight percent based on the total weight of the powder mixture.

7. The process of any one of the preceding Claims wherein the densification aid and the conversion aid are present in amounts sufficient to provide a weight ratio of densification aid to conversion aid of from 1:4 to 8:1.

8. The process of Claim 7 wherein the weight ratio is 1:1 to 1.8:1.

9. The process of any one of the preceding Claims wherein the whisker growth enhancing compound is present in an amount of 0.01 to 5 weight percent based upon the total weight of the powder mixture.

10. The process of any one of the preceding Claims wherein the whisker growth enhancing compound is a non-oxide derivative of calcium.

11. The process of any one of the preceding Claims wherein the whisker growth enhancing compound is an oxide of gallium, indium, hafnium, tantalum or boron.

12. The process of any one of the preceding Claims wherein the powder mixture further comprises silica in an amount of from 2.3 to 6 weight percent based upon total weight of the powder mixture.

13. The process of any one of the preceding Claims wherein the powder mixture further comprises aluminum nitride or boron nitride in an amount of from 0.01 to 5 weight percent based upon the total weight of the powder mixture.

14. The process of any one of the preceding Claims wherein the powder mixture further comprises at least one preformed reinforcing material which is β-silicon nitride in whisker or fiber form, or silicon carbide, titanium carbide, boron carbide, titanium diboride, aluminum oxide or zirconium oxide in whisker, fiber, particle or platelet form, in an amount sufficient to enhance the Palmqvist toughness of the ceramic body.

15. The process of Claim 14 wherein the total of the amount of silicon nitride plus the amount of preformed reinforcing material is from 65 to 99.75 weight percent based on the total weight of the powder mixture.

16. The process of any one of the preceding Claims wherein the powder mixture further comprises at least one preformed, coated reinforcing material which is magnesium oxide, aluminum nitride or mullite, having a coating of silicon carbide, titanium carbide, boron carbide, titanium diboride, aluminum oxide or zirconium oxide, in an amount sufficient to enhance the Palmqvist toughness of the ceramic body, said coated material being in the form of whiskers, fibers, particles or platelets.

17. The process of Claim 16 wherein the total of the amount of silicon nitride plus the amount of preformed, coated reinforcing material is from 65 to 99.75 weight percent based on the total weight of the powder mixture.

18. The process of any one of the preceding Claims wherein the temperature is from 1750 ° C to 1870 ° C.

19. The process of any one of the preceding Claims wherein the pressure is from 3000 psig (20.8 MPa) to 6000 psig (41.5 MPa).

20. The process of any one of the preceding Claims wherein the density of the silicon nitride ceramic is greater than 95 percent of the theoretical value.

21. A silicon nitride ceramic body having a fracture toughness greater than 6 MPa $(m)^{1/2}$ as measured by the Chevron notch technique at 23 ° C, comprising:
(a) a crystalline phase of β-silicon nitride of which at least 20 volume percent, as measured by viewing one plane of the silicon nitride ceramic body by scanning electron photomicrography, is in the form of whiskers having an average aspect ratio of at least 2.5; and
(b) a glassy phase in an amount not greater than 35 weight percent of the total weight comprising a densification aid, a conversion aid, silica, and a beta-silicon nitride whisker growth enhancing compound, said densification aid, a conversion aid and a whisker growth enhancing compound being as defined in Claim 1.

22. The body of Claim 21 wherein the densification aid is beryllium oxide, magnesium oxide, calcium oxide, strontium oxide, tantalum oxide, hafnium oxide, indium oxide, gallium oxide, zinc oxide, barium oxide or radium oxide and the conversion aid is scandium oxide, lanthanum oxide, sodium oxide or actinium oxide, provided that the densification aid is different from the conversion aid.

23. The body of Claim 21 or Claim 22 wherein the glassy phase comprises from 8 to 60 weight percent of the densification aid, from 15 to 64 weight percent of the conversion aid, from 0.1 to 25 weight percent beta-silicon nitride whisker growth enhancing compound, and from 7 to 77 weight percent silica; and wherein the weight ratio of conversion aid to densification aid is from 1:4 to 8:1; and wherein not greater than 10 weight percent of the total weight is present as other phases.

24. The body of Claim 23 wherein one of the other phases is an enstatite which possesses a fiber-like, layered and ordered structure.

25. The body of Claim 24 wherein the enstatite fibers have an average diameter of approximately 500 nanometers and an average length of from 0.7 to 1.0 micrometer.

26. The body of Claim 24 or Claim 25 wherein the silicon nitride whiskers of the crystalline phase are intermixed with the enstatite fibers of the glassy phase.

27. The body of any one of Claims 21 to 26 wherein the glassy phase further comprises aluminum nitride or boron nitride in an amount of from 0.01 to 15.0 weight percent based upon total glassy phase weight.

28. The body of any one of Claims 21 to 27 wherein the glassy phase further comprises at least one preformed reinforcing material which is of β-silicon nitride in whisker or fiber form, or silicon carbide, titanium carbide, boron carbide, titanium diboride, aluminum oxide or zirconium oxide in whisker, fiber, particle or platelet form, in an amount sufficient to enhance the Palmqvist toughness of the body.

29. The body of any one of Claims 21 to 28 wherein the glassy phase further comprises at least one preformed, coated reinforcing material, which is magnesium oxide, aluminum nitride or mullite, and having a coating of silicon carbide, titanium carbide, boron carbide, titanium diboride, aluminum oxide or zirconium oxide, said coated material being in the form of whiskers, fibers, particles or platelets, in an amount sufficient to enhance the Palmqvist toughness.

30. The body of Claim 28 wherein the

(a) has an average diameter of less than 0.2 μm and constitutes up to 10 volume percent of the glassy phase;
(b) has an average diameter of from 0.2 μm to 0.5 μm and constitutes up to 15 volume percent of the glassy phase;
(c) has an average diameter of from 0.5 μm to 1.5 μm and constitutes up to 25 volume percent of the glassy phase;
(d) has an average diameter of from 1.5 μm to 2.5 μm and constitutes up to 30 volume percent of the glassy phase;
(e) has an average diameter of from 2.5 μm to 5.0 μm and constitutes up to 35 volume percent of the glassy phase;
(f) has an average diameter of from 5.0 μm to 15.0 μm and constitutes up to 45 volume percent of the glassy phase;
(g) has an average diameter of from 15.0 μm to 25.0 μm and constitutes up to 50 volume percent of the glassy phase; or
(h) has an average diameter of greater than 25.0 μm and constitutes up to 65 volume percent of the glassy phase.

31. The body of any one of Claims 21 to 30 wherein the percentage of silicon nitride whiskers is at least 35 volume percent.

32. The body of any one of Claims 21 to 31 wherein the fracture toughness is greater than 7 MPa $(m)^{\frac{1}{2}}$.

33. The body of any one of Claims 21 to 32 wherein the fracture toughness as measured by the Chevron notch technique at 1000 °C is from 9 MPa $(m)^{\frac{1}{2}}$ to 14 MPa $(m)^{\frac{1}{2}}$.

34. The body of any one of Claims 21 to 33 wherein the Palmqvist toughness measured at 23 °C is from 37 to 52 kg/mm.

35. A cutting tool fabricated from the body of any one of Claims 21 to 34.

Patentansprüche

1. Verfahren zum Herstellen eines eigenverstärkten Siliciumnitridkeramikkörpers mit einer Bruchzähigkeit von größer als 6 MPa $(m)^{1/2}$ der im wesentlichen β-Siliciumnitridwhisker mit einem hohen mittleren Aspektverhältnis enthält, wobei das Verfahren umfaßt das Behandeln eines Pulvergemischs, umfassend:
(a) Siliciumnitrid in einer Menge, die ausreichend ist, um einen Keramikkörper bereitzustellen;
(b) ein Verdichtungshilfsmittel, wobei das Verdichtungshilfsmittel eine Quelle von (i) einem Gruppe Ia-Element, ausgewählt aus Lithium, Natrium, Kalium, Rubidium, Cäsium und Francium, (ii) einem Gruppe IIa-Element, ausgewählt aus Beryllium, Magnesium, Calcium, Strontium, Barium und Radium; (iii) Zink; (iv) einem Gruppe IIIb-Element, ausgewählt aus Indium und Gallium; (v) Silicium; (vi) einem Gruppe IVa-Element, ausgewählt aus Hafnium und Titan oder (vii) Tantal ist, wobei die Quelle in einer Menge vorliegt, die ausreichend ist, um eine Verdichtung des Pulvers zu fördern;
(c) ein Umwandlungshilfsmittel, wobei das Umwandlungshilfsmittel eine Quelle von (i) einem Gruppe IIIa-Element, ausgewählt aus Scandium, Yttrium, Actinium und Lanthan oder (ii) einem Gruppe Ia-Element, ausgewählt aus Lithium, Natrium, Kalium, Rubidium, Cäsium und Francium ist, wobei die Quelle in einer Menge vorliegt, die ausreichend ist, um die im wesentlichen vollständige Umwandlung des Siliciumnitridausgangsmaterials in β-Siliciumnitrid zu fördern und
(d) mindestens eine Whiskerwachstum erhöhende Verbindung, in einer Menge, die ausreichend ist, um die Bildung von β-Siliciumnitridwhiskern zu fördern, wobei die Verbindung eine Verbindung von (i) einem Gruppe Ia-Element, ausgewählt aus Natrium und Kalium; (ii) Kupfer; (iii) einem Gruppe IIa-Element, ausgewählt aus Strontium, Calcium und Barium; (iv) Zink; (v) einem Gruppe IIIa-Element, ausgewählt aus Scandium und Lanthan; (vi) einem Gruppe IVa-Element, ausgewählt aus Titan und Zirkonium; (vii) einem Gruppe Va-Element, ausgewählt aus Vanadium und Niob; (viii) Chrom; (ix) Mangan; (x) einem Gruppe VIII-Element, ausgewählt aus Eisen, Kobalt und Nickel oder Gemischen von zwei oder mehr davon oder ein Oxid eines Gruppe IIIb-Elements, ausgewählt aus Indium, Gallium und Bor; Hafnium oder Tantal ist,

wobei (b), (c) und (d) aus drei verschiedenen Elementen stammen und vorausgesetzt ist, daß:

(1) wenn das Pulvergemisch ein Oxid eines Gruppe IIIa-Elements enthält, es nicht auch ein Nitrid oder Oxynitrid eines Gruppe IIa- oder Gruppe IIIb-Elements enthält;
(2) wenn das Pulvergemisch ein Nitrid oder Oxynitrid eines Gruppe IIIa-Elements enthält, es nicht auch ein Oxid, Nitrid oder Oxynitrid eines Gruppe IIa-Elements oder ein Nitrid oder Oxynitrid eines Gruppe IIIb-Elements enthält;
(3) wenn das Pulvergemisch eine Quelle von Zink, Titan, Indium, Gallium, Hafnium oder Tantal enthält, es nicht auch freies Siliciumdioxid enthält und
(4) wenn das Pulvergemisch sowohl ein Magnesiumderivat als Verdichtungshilfsmittel als auch ein Yttriumderivat als Umwandlungshilfsmittel enthält, es auch mindestens ein vorgeformtes verstärkendes Material enthält, ausgewählt aus β-Siliciumnitrid in Whisker- oder Faserform und Siliciumcarbid, Titancarbid, Borcarbid, Titandiborid, Aluminiumoxid oder Zirkoniumoxid in Whisker-, Faser-, Teilchen- oder Plättchenform, in einer Menge, die ausreichend ist, um die Palmqvist-Zähigkeit des Keramikkörpers zu erhöhen,

mit Temperatur- und Druckbedingungen, die ausreichend sind, daß eine Verdichtung und in situ Bildung von β-Siliciumnitridwhiskern mit einem mittleren Aspektverhältnis von mindestens 2,5 stattfindet und ausreichend, daß der Siliciumnitridkeramikkörper, der gebildet wird, eine Bruchzähigkeit von größer als 6 MPa $(m)^{1/2}$ aufweist.

2. Verfahren nach Anspruch 1, worin die β-Siliciumnitridwhisker ein Aspektverhältnis von 2 bis 16 aufweisen und in einer Menge von mindestens 20 Volumenprozent vorliegen, gemessen durch Betrachten einer Ebene des Siliciumnitridkeramikkörpers durch Rasterelektronenmikroskopie.

3. Verfahren nach Anspruch 1 oder 2, worin das Siliciumnitridausgangsmaterial nicht mehr als 10 Gew.-% β-Siliciumnitrid enthält.

4. Verfahren nach einem der vorhergehenden Ansprüche, worin das Verdichtungshilfsmittel in einer Menge von 0,05 bis 27,0 Gew.-% basierend auf dem Gesamtgewicht des Pulvergemischs vorliegt.

5. Verfahren nach einem der vorhergehenden Ansprüche, worin das Verdichtungshilfsmittel ausgewählt ist aus Oxiden von Strontium, Calcium oder Natrium.

6. Verfahren nach einem der vorhergehenden Ansprüche, worin das Umwandlungshilfsmittel in einer Menge von 0.2 bis 29,5 Gew.-%, basierend auf dem Gesamtgewicht des Pulvergemischs, vorliegt.

7. Verfahren nach einem der vorhergehenden Ansprüche, worin das Verdichtungshilfsmittel und das Umwandlungshilfsmittel in Mengen vorliegen, die ausreichend sind, um ein Gewichtsverhältnis von Verdichtungshilfsmittel zu Umwandlungshilfsmittel von 1:4 bis 8:1 bereitzustellen.

8. Verfahren nach Anspruch 7, worin das Gewichtsverhältnis 1:1 bis 1,8:1 ist.

9. Verfahren nach einem der vorhergehenden Ansprüche, worin die Whiskerwachstum erhöhende Verbindung in einer Menge von 0,01 bis 5 Gew.-%, basierend auf dem Gesamtgewicht des Pulvergemischs vorliegt.

10. Verfahren nach einem der vorhergehenden Ansprüche, worin die Whiskerwachstum erhöhende Verbindung eine Nichtoxidverbindung von Calcium ist.

11. Verfahren nach einem der vorhergehenden Ansprüche, worin die Whiskerwachstum erhöhende Verbindung ein Oxid von Gallium, Indium, Hafnium, Tantal oder Bor ist.

12. Verfahren nach einem der vorhergehenden Ansprüche, worin das Pulvergemisch weiterhin Siliciumdioxid in einer Menge von 2,3 bis 6 Gew.-%, basierend auf dem Gesamtgewicht des Pulvergemischs, umfaßt.

13. Verfahren nach einem der vorhergehenden Ansprüche, worin das Pulvergemisch weiterhin Aluminiumnitrid oder Bornitrid in einer Menge von 0,01 bis 5 Gew.-%, basierend auf dem Gesamtgewicht des Pulvergemischs umfaßt.

14. Verfahren nach einem der vorhergehenden Ansprüche, worin das Pulvergemisch weiterhin mindestens ein vorgeformtes verstärkendes Material umfaßt, welches β-Siliciumnitrid in Whisker- oder Faserform oder Siliciumcarbid, Titancarbid, Borcarbid, Titandiborid, Aluminiumoxid oder Zirkoniumoxid in Whisker-, Faser-, Teilchen- oder Plättchenform ist, in einer Menge, die ausreichend ist, um die Palmqvist-Zähigkeit des Keramikkörpers zu erhöhen.

15. Verfahren nach Anspruch 14, worin die gesamte Menge von Siliciumnitrid plus die Menge des vorgeformten verstärkenden Materials von 65 bis 99,75 Gew.-%, basierend auf dem Gesamtgewicht des Pulvergemischs ist.

16. Verfahren nach einem der vorhergehenden Ansprüche, worin das Pulvergemisch weiterhin mindestens ein vorgeformtes, beschichtetes verstärkendes Material umfaßt, welches Magnesiumoxid, Aluminiumnitrid oder Mullit ist, mit einer Beschichtung von Siliciumcarbid, Titancarbid, Borcarbid, Titandiborid, Aluminiumoxid oder Zirkoniumoxid, in einer Menge, die ausreichend ist, um die Palmqvist-Zähigkeit des Keramikkörpers zu erhöhen, wobei das beschichtete Material in der Form von Whiskern, Fasern, Teilchen oder Plättchen vorliegt.

17. Verfahren nach Anspruch 16, worin die gesamte Menge von Siliciumnitrid plus die Menge von vorgeformtem, beschichtetem verstärkendem Material von 65 bis 99,75 Gew.-%, basierend auf dem Gesamtgewicht des Pulvergemischs ist.

18. Verfahren nach einem der vorhergehenden Ansprüche, worin die Temperatur von 1750 °C bis 1870 °C ist.

19. Verfahren nach einem der vorhergehenden Ansprüche, worin der Druck von 3000 psig (20,8 MPa) bis 6000 psig (41,5 MPa) ist.

20. Verfahren nach einem der vorhergehenden Ansprüche, worin die Dichte der Siliciumnitridkeramik größer als 95 Prozent des theoretischen Werts ist.

21. Siliciumnitridkeramikkörper mit einer Bruchzähigkeit von größer als 6 MPa $(m)^{1/2}$, gemessen durch die Chevron-Kerbetechnik bei 23 °C, umfassend:
(a) eine kristalline Phase von β-Siliciumnitrid, von welcher mindestens 20 Volumenprozent, gemessen durch Betrachten einer Ebene des Siliciumnitridkeramikkörpers durch Rasterelektronenmikroskopie, in der Form von Whiskern mit einem mittleren Aspektverhältnis von mindestens 2,5 ist und
(b) eine galasartige Phase, in einer Menge von nicht größer als 35 Gew.-% des Gesamtgewichts, umfassend ein Verdichtungshilfsmittel, ein Umwandlungshilfsmittel, Siliciumdioxid und eine β-Siliciumnitridwhiskerwachstum erhöhende Verbindung, wobei das Verdichtungshilfsmittel, ein Umwandlungshilfsmittel und eine Whiskerwachstum erhöhende Verbindung wie in Anspruch 1 definiert sind.

22. Körper von Anspruch 21, worin das Verdichtungshilfsmittel Berylliumoxid, Magnesiumoxid, Calciumoxid, Strontiumoxid, Tantaloxid, Hafniumoxid, Indiumoxid, Galliumoxid, Zinkoxid, Bariumoxid oder Radiumoxid ist und das Umwandlungshilfsmittel Scandiumoxid, Lanthanoxid, Natriumoxid oder Actiniumoxid ist, vorausgesetzt, daß das Verdichtungshilfsmittel von dem Umwandlungshilfsmittel verschieden ist.

23. Körper nach Anspruch 21 oder Anspruch 22, worin die glasartige Phase von 8 bis 60 Gew.-% des Verdichtungshilfsmittels, von 15 bis 64 Gew.-% des Umwandlungshilfsmittels, von 0,1 bis 25 Gew.-% β-Siliciumnitridwhiskerwachstum erhöhende Verbindung und von 7 bis 77 Gew.-% Siliciumdioxid umfaßt und worin das Gewichtsverhältnis von Umwandlungshilfsmittel zu Verdichtungshilfsmittel von 1:4 bis 8:1 ist und worin nicht mehr als 10 Gew.-% des Gesamtgewichts als andere Phasen vorliegen.

24. Körper nach Anspruch 23, worin eine der anderen Phasen ein Enstatit ist, der eine faserähnliche, geschichtete oder geordnete Struktur besitzt.

25. Körper nach Anspruch 24, worin die Entstatitfasern einen mittleren Durchmesser von ungefähr 500 Nanometer und eine mittlere Länge von 0,1 bis 1,0 Mikrometer haben.

26. Körper nach Anspruch 24 oder Anspruch 25, worin die Siliciumnitridwhisker der kristallinen Phase mit den Enstatitfasern der glasartigen Phase vermischt sind.

27. Körper nach einem der Ansprüche 21 bis 26, worin die glasartige Phase weiterhin Aluminiumnitrid oder Bornitrid in einer Menge von 0,01 bis 15,0 Gew.-%, basierend auf dem Gesamtgewicht der glasartigen Phase, umfaßt.

28. Körper nach einem der Ansprüche 21 bis 27, worin die glasartige Phase weiterhin mindestens ein vorgeformtes verstärkendes Material umfaßt, welches aus β-Siliciumnitrid in Whisker- oder Faserform oder Siliciumcarbid, Titancarbid, Borcarbid, Titandiborid, Aluminiumoxid oder Zirkoniumoxid in Whisker-, Faser-, Teilchen- oder Plättchenform ist, in einer Menge, die ausreichend ist, um die Palmqvist-Zähigkeit des Körpers zu erhöhen.

29. Körper nach einem der Ansprüche 21 bis 28, worin die glasartige Phase weiterhin mindestens ein vorgeformtes beschichtetes verstärkendes Material umfaßt, welches Magnesiumoxid, Aluminiumnitrid oder Mullit ist und eine Beschichtung aus Siliciumcarbid, Titancarbid, Borcarbid, Titandiborid, Aluminiumoxid oder Zirkoniumoxid hat, wobei das beschichtete Material in der Form von Whiskern, Fasern, Teilchen oder Plättchen ist, in einer Menge, die ausreichend ist, um die Palmqvist-Zähigkeit zu erhöhen.

30. Körper nach Anspruch 28, worin das verstärkende Material:
    (a) einen mittleren Durchmesser von weniger als 0,2 μm hat und bis zu 10 Volumenprozent der glasartigen Phase bildet;
    (b) einen mittleren Durchmesser von 0,2 μm bis 0,5 μm hat und bis zu 15 Volumenprozent der glasartigen Phase bildet;
    (c) einen mittleren Durchmesser von 0,5 μm bis 1,5 μm hat und bis zu 25 Volumenprozent der glasartigen Phase bildet;
    (d) einen mittleren Durchmesser von 1,5 μm bis 2,5 μm hat und bis zu 30 Volumenprozent der glasartigen Phase bildet;
    (e) einen mittleren Durchmesser von 2,5 μm bis 5,0 μm hat und bis zu 35 Volumenprozent der glasartigen Phase bildet;
    (f) einen mittleren Durchmesser von 5,0 μm bis 15,0 μm hat und bis zu 45 Volumenprozent der glasartigen Phase bildet;
    (g) einen mittleren Durchmesser von 15,0 μm bis 25,0 μm hat und bis zu 50 Volumenprozent der glasartigen Phase bildet oder
    (h) einen mittleren Durchmesser von größer als 25,0 μm hat und bis zu 65 Volumenprozent der glasartigen Phase bildet.

31. Körper nach einem der Ansprüche 21 bis 30, worin der Prozentanteil von Siliciumnitridwhiskern mindestens 35 Volumenprozent ist.

32. Körper nach einem der Ansprüche 21 bis 31, worin die Bruchzähigkeit größer als 7 MPa $(m)^{1/2}$ ist.

33. Körper nach einem der Ansprüche 21 bis 32, worin die Bruchzähigkeit, gemessen durch die Chevron-Kerbetechnik bei 1000 °C von 9 MPa $(m)^{1/2}$ bis 17 MPa $(m)^{1/2}$ ist.

34. Körper nach einem der Ansprüche 21 bis 33, worin die Palmqvist-Zähigkeit, gemessen bei 23 °C von 37 bis 52 kg/mm ist.

35. Schneidewerkzeug, das aus dem Körper nach einem der Ansprüche 21 bis 34 hergestellt ist.

Revendications

1. Procédé pour la préparation d'un corps céramique auto-renforcé en nitrure de silicium ayant une ténacité à la rupture supérieure à 6 MPa.$(m)^{1/2}$, et contenant de manière prédominante des trichites de nitrure de silicium β ayant un rapport d'aspect moyen élevé. Le procédé consiste à soumettre un mélange en poudre comprenant:
    (a) du nitrure de silicium en une quantité suffisante pour fournir un corps céramique

(b) un aide à la densification, ledit aide à la densification étant une source (i) d'un élément du groupe Ia choisi parmi le lithium, le sodium, le potassium, le rubidium, le césium, et le francium; (ii) d'un élément du groupe IIa choisi parmi le béryllium, le magnésium, le calcium, le strontium, le baryum, et le radium; (iii) du zinc; (iv) d'un élément du groupe IIIb choisi parmi l'indium et le gallium; (v) du silicium; (vi) d'un élément du groupe IVa choisi parmi le hafnium et le titane; ou (vii) du tantale, ladite source étant présente en une quantité suffisante pour favoriser la densification de la poudre;

(c) un aide à la conversion, ledit aide à la conversion étant une source (i) d'un élément du groupe IIIa choisi parmi le scandium, l'yttrium, l'actinium, et le lanthane; ou (ii) d'un élément du groupe Ia choisi parmi le lithium, le sodium, le potassium, le rubidium, le césium et le francium, ladite source étant présente en une quantité suffisante pour favoriser la conversion essentiellement complète du nitrure de silicium en nitrure de silicium β; et

(d) au moins un composé améliorant la croissance de trichites en une quantité suffisante pour favoriser la formation de trichites de nitrure de silicium β, ledit composé étant un dérivé (i) d'un élément du groupe Ia choisi parmi le sodium et le potassium; (ii) du cuivre; (iii) d'un élément du groupe IIa choisi parmi le strontium, le calcium et le baryum; (iv) du zinc; (v) d'un élément du groupe IIIa choisi parmi le scandium et le lanthane; (vi) d'un élément du groupe IVa choisi parmi le titane et le zirconium; (vii) d'un élément du groupe Va choisi parmi le vanadium et le niobium; (viii) du chrome; (ix) du manganèse; (x) d'un élément du groupe VIII choisi parmi le fer, le cobalt, et le nickel; ou des mélanges de ceux-ci, ou un oxyde d'un élément du groupe IIIb choisi parmi l'indium, le gallium et le bore; du hafnium, ou du tantale;

(b), (c) et (d) étant dérivés de trois éléments différents et pourvu que:

(1) quand le mélange en poudre contient un oxyde d'un élément du groupe IIIa, il ne contienne pas également un nitrure ou un oxynitrure d'un élément du groupe IIa ou du groupe IIIb;

(2) quand le mélange en poudre contient un nitrure ou un oxynitrure d'un élément du groupe IIIa, il ne contienne pas également un oxyde, un nitrure ou un oxynitrure d'un élément du groupe IIa ou un nitrure ou un oxynitrure d'un élément du groupe IIIb;

(3) quand le mélange en poudre contient une source de zinc, de titane, d'indium, de gallium, de hafnium ou de tantale, il ne contiennent pas également de dioxyde de silicium libre; et

(4) quand le mélange en poudre contient à la fois un dérivé de magnésium en tant qu'aide à la densification et un dérivé d'yttrium en tant qu'aide à la conversion, il contienne également au moins une matière de renforcement préformée choisie parmi un nitrure de silicium β sous forme de trichites ou de fibres, et du carbure de silicium, du carbure de titane, du carbure de bore, du diborure de titane, de l'oxyde d'aluminium ou de l'oxyde de zirconium sous forme de trichites, de fibres, de particules ou de plaquettes, en une quantité suffisante pour améliorer la ténacité Palmqvist du corps céramique;

dans des conditions de température et de pression suffisantes de façon que se produisent la densification et la formation in situ de trichites de nitrure de silicium β ayant un rapport d'aspect moyen d'au moins 2,5 et de façon telle que le corps céramique en silicium ait une ténacité à la rupture supérieure à 6 MPa $(m)^{1/2}$.

2. Procédé selon la revendication 1, dans lequel les trichites de nitrure de silicium β ont un rapport d'aspect de 2 à 16 et sont présentes en une quantité d'au moins 20% en volume, mesuré en visualisant un plan du corps céramique en nitrure de silicium par micrographie électronique à balayage.

3. Procédé selon la revendication 1 ou 2, dans lequel le nitrure de silicium de départ ne contient pas plus de 10% en poids de nitrure de silicium β.

4. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'aide à la densification est présent en une quantité de 0,05 à 27,0% en poids par rapport au poids total du mélange en poudre.

5. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'aide à la densification est choisi parmi des oxydes de strontium, de calcium ou de sodium.

6. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'aide à la conversion est présent en une quantité de 0,2 à 29,5% en poids par rapport au poids total du mélange en poudre.

7. Procédé selon l'une quelconque des revendications précédentes, dans lequel l'aide à la densification et l'aide à la conversion sont présents en quantités suffisantes pour fournir un rapport pondéral de l'aide à la densification à l'aide à la conversion de 1:4 à 8:1.

8. Procédé selon la revendication 7, dans lequel le rapport pondéral est de 1:1 à 1,8:1.

9. Procédé selon l'une quelconque des revendications précédentes, dans lequel le composé d'amélioration à la croissance de trichites est présent en une quantité de 0,01 à 5% en poids par rapport au poids total du mélange en poudre.

10. Procédé selon l'une quelconque des revendications précédentes, dans lequel le composé d'amélioration à la croissance de trichites est un dérivé non oxyde de calcium.

11. Procédé selon l'une quelconque des revendications précédentes, dans lequel le composé d'amélioration à la croissance de trichites est un oxyde de gallium, d'indium, de hafnium, de tantale ou de bore.

12. Procédé selon l'une quelconque des revendications précédentes, dans lequel le mélange en poudre comprend de plus de la silice en une quantité de 2,3 à 6% en poids par rapport au poids total du mélange en poudre.

13. Procédé selon l'une quelconque des revendications précédentes, dans lequel le mélange en poudre comprend de plus du nitrure d'aluminium ou du nitrure de bore en une quantité de 0,01 à 5% en poids par rapport au poids total du mélange en poudre.

14. Procédé selon l'une quelconque des revendications précédentes, dans lequel le mélange en poudre comprend de plus au moins une matière de renforcement préformée qui est du nitrure de silicium β sous forme de trichite ou de fibre, ou du carbure de silicium, du carbure de titane, du carbure de bore, du diborure de titane, de l'oxyde d'aluminium ou de l'oxyde de zirconium sous forme de trichites, de fibres, de particules ou de plaquettes, en une quantité suffisante pour améliorer la ténacité Palmqvist du corps céramique.

15. Procédé selon la revendication 14, dans lequel le total de la quantité de nitrure de silicium plus la quantité de la matière de renforcement préformée est de 65 à 99,75% en poids par rapport au poids total du mélange en poudre.

16. Procédé selon l'une quelconque des revendications précédentes, dans lequel le mélange en poudre comprend de plus au moins une matière de renforcement revêtue, préformée qui est un oxyde de magnésium, un nitrure d'aluminium ou une mullite, ayant un revêtement de carbure de silicium, de carbure de titane, de carbure de bore, de diborure de titane, d'oxyde d'aluminium ou d'oxyde de zirconium, en une quantité suffisante pour améliorer la ténacité Palmqvist du corps céramique, ladite matière revêtue étant sous forme de trichites, de fibres, de particules ou de plaquettes.

17. Procédé selon la revendication 16, dans lequel le total de la quantité de nitrure de silicium plus la quantité de matière de renforcement revêtue, préformée est de 65 à 99,75% en poids par rapport au poids total du mélange en poudre.

18. Procédé selon l'une quelconque des revendications précédentes, dans lequel la température est de 1 750 °C à 1 870 °C.

19. Procédé selon l'une quelconque des revendications précédentes, dans lequel la pression est de 20,8 MPa (3 000 psig) à 41,5 MPa (6 000 psig).

20. Procédé selon l'une quelconque des revendications précédentes, dans lequel la densité de la céramique en nitrure de silicium est supérieure à 95% de la valeur théorique.

21. Corps céramique en nitrure de silicium ayant une ténacité à la rupture supérieure à 6 MPa.$(m)^{1/2}$, mesurée par la technique avec encoche en chevron décrite ci-dessous, comprenant:

(a) une phase cristalline de nitrure de silicium β dont au moins 20% en volume, mesuré en visualisant un plan du corps céramique en nitrure de silicium par microscope électronique à balayage, est sous forme de trichites ayant un rapport d'aspect moyen d'au moins 2,5; et
(b) une phase vitreuse, en une quantité ne dépassant pas 35% en poids du poids total, comprenant un aide à la densification, un aide à la conversion, de la silice, et un composé améliorant la croissance de trichites tels que définis dans la revendication 1.

22. Corps selon la revendication 21, dans lequel l'aide à la densification est de l'oxyde de béryllium, de l'oxyde de magnésium, de l'oxyde de calcium, de l'oxyde de strontium, de l'oxyde de tantale, de l'oxyde de hafnium, de l'oxyde d'indium, de l'oxyde de gallium, de l'oxyde de zinc, de l'oxyde de baryum ou de l'oxyde de radium et l'aide à la conversion est de l'oxyde de scandium, de l'oxyde de lanthane, de l'oxyde de sodium ou de l'oxyde d'actinium, pourvu que l'aide à la densification soit différent de l'aide à la conversion.

23. Corps selon la revendication 21 ou la revendication 22, dans lequel la phase vitreuse comprend de 8 à 60% en poids de l'aide à la densification, de 15 à 64% en poids de l'aide à la conversion, de 0,1 à 25% en poids de composé améliorant la croissance de trichites de nitrure de silicium β, et de 7 à 77% en poids de silice; et dans lequel le rapport pondéral d'aide à la conversion à l'aide à la densification est de 1:4 à 8:1, et dans lequel pas plus de 10% en poids du poids total n'est présent sous forme d'autres phases.

24. Corps de la revendication 23, dans lequel l'une des autres phases est une enstatite qui possède une structure sous forme de fibres, en couche et ordonnée.

25. Corps de la revendication 24, dans lequel les fibres d'enstatite possèdent un diamètre moyen d'approximativement 500 nanomètres et une longueur moyenne de 0,7 à 1,0 micromètre.

26. Corps selon la revendication 24 ou la revendication 25, dans lequel les trichites de nitrure de silicium de la phase cristalline sont entremêlées avec les fibres d'enstatite de la phase vitreuse.

27. Corps selon l'une quelconque des revendications 21 à 26, dans lequel la phase vitreuse comprend de plus du nitrure d'aluminium ou du nitrure de bore en une quantité de 0,01 à 15,0% en poids par rapport au poids total de la phase vitreuse.

28. Corps selon l'une quelconque des revendications 21 à 27, dans lequel la phase vitreuse comprend de plus au moins une matière de renforcement préformée qui est du nitrure de silicium β sous forme de trichites ou de fibres, ou du carbure de silicium, du carbure de titane, du carbure de bore, du diborure de titane, de l'oxyde d'aluminium ou de l'oxyde de zirconium sous forme de trichites, de fibres, de particules ou de plaquettes, en une quantité suffisante pour améliorer la ténacité Palmqvist du corps.

29. Corps selon l'une quelconque de revendications 21 à 28, dans lequel la phase vitreuse comprend de plus au moins une matière de renforcement revêtue, préformée, qui est de l'oxyde de magnésium, du nitrure d'aluminium ou de la mullite, et possédant un revêtement de carbure de silicium, de carbure de titane, de carbure de bore, de diborure de titane, d'oxyde d'aluminium ou d'oxyde de zirconium, ladite matière revêtue étant sous forme de trichites, de fibres, de particules ou de plaquettes, en une quantité suffisante pour améliorer la ténacité Palmqvist.

30. Corps selon la revendication 28, dans lequel la matière de renforcement:
(a) possède un diamètre moyen inférieur à 0,2 μm et constitue jusqu'à 10% en volume de la phase vitreuse;
(b) possède un diamètre moyen de 0,2 μm à 0,5 μm et constitue jusqu'à 15% en volume de la phase vitreuse;
(c) possède un diamètre moyen de 0,5 μm à 1,5 μm et constitue jusqu'à 25% en volume de la phase vitreuse;
(d) possède un diamètre moyen de 1,5 μm à 2,5 μm et constitue jusqu'à 30% en volume de la phase vitreuse;
(e) possède un diamètre moyen de 2,5 μm à 5,0 μm et constitue jusqu'à 35% en volume de la phase vitreuse;

(f) possède un diamètre moyen de 5,0 µm à 15,0 µm et constitue jusqu'à 45% en volume de la phase vitreuse;
(g) possède un diamètre moyen de 15,0 µm à 25,0 µm et constitue jusqu'à 50% en volume de la phase vitreuse;
(h) possède un diamètre moyen supérieur à 25,0 µm et constitue jusqu'à 65% en volume de la phase vitreuse;

31. Corps selon l'une quelconque des revendications 21 à 30, dans lequel le pourcentage de trichites de nitrure de silicium est d'au moins 35% en volume.

32. Corps selon l'une quelconque des revendications 21 à 31, dans lequel la ténacité à la rupture est supérieure à 7 $MPa.(m)^{1/2}$.

33. Corps selon l'une quelconque des revendications 21 à 32, dans lequel la ténacité à la rupture mesurée par la technique avec encoche en chevron à 1 000 °C est de 9 $MPa.(m)^{1/2}$ à 14 $MPa.(m)^{1/2}$.

34. Corps selon l'une quelconque des revendications 21 à 33, dans lequel la ténacité Palmqvist mesurée à 23 °C est de 37 à 52 kg/mm.

35. Outil de coupe fabriqué à partir du corps selon l'une quelconque des revendications 21 à 34.